
(12) UK Patent Application (19) GB (11) 2 127 013 A

(21) Application No 8318335
(22) Date of filing 6 Jul 1983
(30) Priority data
(31) 8226596
(32) 17 Sep 1982
(33) United Kingdom (GB)
(43) Application published
4 Apr 1984
(51) INT CL³
C07C 33/46 69/63

(52) Domestic classification
C2C 220 227 22Y 234
240 311 31Y 360 361 366
368 36Y 37X 491 505
509 50Y 633 638 652 658
65X 697 778 AA BZ WS
U1S 1347 C2C

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(58) Field of search
C2C

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(54) Tetrafluoroterephthalyl alcohol,
esters thereof and a process for
their preparation

(57) Tetrafluoroterephthalyl alcohol
and its esters, useful in the synthesis
of pesticidal compounds, are prepared
by reducing a tetrafluoroterephthaloyl

halide, especially the chloride, with
suitably, sodium borohydride in
diglyme, followed, as appropriate, by
esterification. The alcohol and its
esters can be further reduced by
catalytic hydrogenation under mild
conditions to yield tetrafluoro-p-
xylene or the intermediate 4-methyl-
2,3,5,6-tetrafluorobenzyl alcohol.

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The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

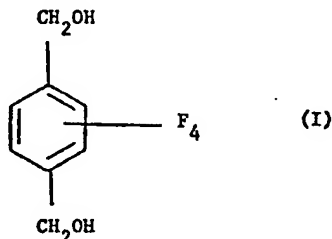
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SPECIFICATION

Tetrafluoroterephthalyl alcohol, esters thereof and a process for their preparation

This invention relates to tetrafluoroterephthalyl alcohol and esters thereof, which are useful chemical intermediates in the synthesis of pesticidal compounds, and a process for their preparation.

According to one aspect of the invention, there is provided a novel compound having the chemical formula (I):



which is 2,3,5,6-tetrafluoroterephthalyl alcohol, and esters thereof.

The esters of tetrafluoroterephthalyl alcohol may be mono- or di-esters formed by reaction with organic or inorganic oxygen acids using conventional esterification techniques. In particular, there are mentioned esters formed from carboxylic acids such as acetic acid and especially, trifluoroacetic acid, and from p-toluenesulphonic acid.

In another aspect of the invention a process is provided for the preparation of 2,3,5,6-tetrafluoroterephthalyl alcohol and esters thereof, which comprises reducing a 2,3,5,6-tetrafluoroterephthaloyl halide, especially the chloride, and, to form the esters, esterifying the alcohol so obtained with an organic or inorganic oxygen acid.

It has been found that the reduction can be performed satisfactorily, without loss of ring fluorine substituents, using sodium borohydride in diglyme at room temperature. It is envisaged, however, that other covalent hydrides might be used, for instance, other alkali metal borohydrides and aluminium hydrides, in other solvents at different temperatures. It is also envisaged that other types of reducing agents might be used and that the reduction might be achieved by catalytic hydrogenation.

The starting material, tetrafluoroterephthaloyl chloride, is a known compound (Chemical Abstracts Service Registry No. 15041-74-4) and may be prepared by treating tetrafluoroterephthalic acid with, for example, thionyl chloride or phosphorus pentachloride. Tetrafluoroterephthalic acid and a method of preparing it are described in the Journal of the Chemical Society (1961), 813 and 1574. It may also be prepared by the acid hydrolysis of tetrafluoroterephthalodinitrile obtained by fluorinating the corresponding tetrachlorinated

compound with potassium fluoride in a polar aprotic solvent. Tetrachloroterephthalodinitrile is obtained from the commercially available tetrachloroterephthaloyl chloride by treatment with aqueous ammonia to give the diamine followed by dehydration using phosphorus oxychloride.

Tetrafluoroterephthalyl alcohol and its esters are precursors of 4-methyl-2,3,5,6-tetrafluorobenzyl alcohol and 4-methyl-2,3,5,6-tetrafluorobenzyl halides which are useful for preparing pesticidal esters.

4-Methyl-2,3,5,6-tetrafluorobenzyl alcohol may be obtained from tetrafluoroterephthalyl alcohol or its esters by partial reduction using, for example, a controlled catalytic hydrogenation process.

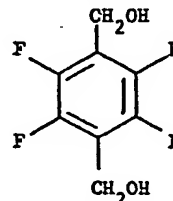
4-Methyl-2,3,5,6-tetrafluorobenzyl halides may be obtained by reducing, by catalytic hydrogenation, both side chains of tetrafluoroterephthalyl alcohol or an ester thereof, to form tetrafluoro-p-xylene which is then selectively halogenated by, for example, the procedure described in German patent 478084. The reduction may proceed more easily when using an ester of tetrafluoroterephthalyl alcohol, especially the trifluoroacetate or tosylate.

The invention is illustrated by the following Example.

Example**Preparation of tetrafluoroterephthalyl alcohol from tetrafluoroterephthaloyl chloride**

A solution of sodium borohydride (10.12 g) in dry diglyme (350 ml) was added dropwise over two hours to a solution of tetrafluoroterephthaloyl chloride (36.6 g) in dry diglyme (75 ml) at a temperature maintained at about 20°C. The resulting reaction mixture was stirred at room temperature for sixteen hours and then drowned into an ice/water mixture (3 l). Three ether extracts (1 x 500 ml; 2 x 1000 ml) were combined and washed with water (2 x 750 ml), sodium bicarbonate solution (1 x 500 ml) and again with water (1 x 750 ml). The washed ether extracts were dried over magnesium sulphate, filtered and evaporated to dryness giving a product (18.0 g), subsequently shown to be tetrafluoroterephthalyl alcohol, in a yield of 64.4% theory.

Analysis of the product by glc-mass spectrometry showed a molecular ion at m/e 210 and fragments at 209, 193, 189, 163 and 145, which is consistent with the structure:

**Preparation of tetrafluoroterephthalyl acetate from tetrafluoroterephthalyl alcohol**

A stoichiometric excess of acetyl chloride (8 ml) was slowly added to tetrafluoroterephthalyl

- alcohol (6 g) in boiling tube. A vigorous reaction was at first observed, with large amounts of gas being evolved, and the temperature rose to 40°C. After gas evolution had ceased and the
- 5 temperature had dropped, some solid material remained. The reaction mixture was then warmed and kept at 35°C until it became clear and no more gas was evolved, and poured into water (50 ml), forming a white precipitate.
- 10 Three ether extracts (100 ml each) were dried over magnesium sulphate, filtered and evaporated to leave a product (8.5 g), subsequently shown to be tetrafluoroterephthalyl acetate containing a few minor impurities, in a yield of 99.7% theory.

15 Claims

1. 2,3,5,6-Tetrafluoroterephthalyl alcohol and esters thereof.
2. A process for the preparation of 2,3,5,6-tetrafluoroterephthalyl alcohol and esters thereof,
- 20 which comprises reducing a 2,3,5,6-tetrafluoroterephthaloyl halide and, to form the esters, esterifying the alcohol so obtained with an organic or inorganic oxygen acid.
3. A process for the preparation of 2,3,5,6-
- 25 tetrafluoroterephthalyl alcohol and esters thereof substantially as herein described with reference to the Example.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1984. Published by the Patent Office,
25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.